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WRIGHT
STATE

Wright State University
Dayton, Ohio 45435

RECEIVED

MAR 1 1982

US EPA CENTRAL REGIONAL LAB.
535 S. CLARK STREET
CHICAGO, ILLINOIS 60605

A. 2
3/16/82
Brehm Laboratory
513/873-2202

153880

March 16, 1982

Mr. Curtis Ross
United States Environmental Protection Agency
Region V
230 S. Dearborn
Chicago, Illinois 60604

Re: EPA Order #56606NAEX

Dear Mr. Ross:

As you know, the samples of leachate received in our laboratory on January 14, 1982 under the subject EPA Order No., have been analyzed for chlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans (CDFs), and these data were reported to you in a telephone conversation by Dr. T.O. Tiernan on February 25, 1982. The purpose of this interim report is to confirm in writing the data on CDDs/CDFs which was verbally transmitted as indicated above, and to provide you with the details of the analytical procedures employed, as well as copies of the original Gas Chromatographic-Mass Spectrometric data obtained in these analyses.

Table 1, which is attached, lists the samples which were received, along with a brief description of each of the samples. Table 2, which is also attached, indicates the concentrations of CDDs/CDFs determined to be present in each of the five water samples which were submitted by EPA. As can be seen from the data in Table 2, no detectable tetrachlorodibenzo-p-dioxins (TCDDs), tetrachlorodibenzofurans (TCDFs), pentachlorodibenzo-p-dioxins (PCDDs) or pentachlorodibenzofurans (PCDFs) were found in these aqueous samples. However, higher chlorinated dioxins and furans [hexachlorinated dibenzo-p-dioxins (HxCDDs), hexachlorodibenzofurans (HxCDFs), heptachlorodibenzo-p-dioxins (HpCDDs), heptachlorodibenzofurans (HpCDFs), octachlorodibenzo-p-dioxin (OCDD), and octachlorodibenzofuran (OCDF)] were detected in three of the five samples. The concentrations of the higher chlorinated CDDs/CDFs ranged from 4.5 picograms/ml (4.5 parts-per-trillion, 4.5 ppt) to 2,693 ppt, among the three samples which were found to contain CDDs/CDFs. Whether or not the CDDs/CDFs are present as solutes or are associated with suspended particulate matter in these samples cannot be determined on the basis of the present results. Copies of the original data obtained in these determinations are appended to this interim report (see Attachment 1). Figures showing mass chromatographic data pertinent to each of the 5 samples, as well as representative GC-MS results obtained for calibration standards, are included in each of the six sections in Attachment 1. Labelling of the

figures for this report has been abbreviated to permit rapid submission of this data. At the top of each figure are listed the nominal masses which correspond to the respective analog signals displayed in that figure. By referring to Table 3, one can determine the ion masses monitored as indicators of each class of CDDs/CDFs.

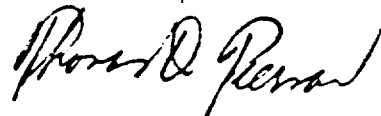
Invariably, analyses of complex environmental samples for CDDs and CDFs is a research project until the optimum technique is developed. Although an established Brehm Laboratory protocol has been developed for preparing and analyzing aqueous samples similar to those submitted by EPA under this Order No., initial attempts to implement these "established" methods yielded results which were not acceptable. This indicated the need to modify the established procedures in order to adequately analyze these specific samples. The analytical methodology employed for these analyses is outlined in detail in Attachment 2. However, a few general comments are in order regarding the procedures employed. Initially, each of the approximately 3000 mL samples were agitated to suspend fine particulate matter contained therein in an effort to ensure sample homogeneity. A 100 mL aliquot of the sample was immediately removed at this point, and transferred to a 250 mL precleaned flint glass bottle, equipped with a Teflon-lined cap. Microliter quantities of solutions containing the internal standards utilized in these analyses, $^{37}\text{Cl}_4$ -2,3,7,8-TCDD, $^{37}\text{Cl}_4$ -1,2,3,4,6,7,8-HpCDD, and $^{37}\text{Cl}_8$ -OCDD, were then added to each of the samples. Subsequently, the samples were prepared and analyzed as described in Attachment 2. It must be emphasized that not all of the possible CDDs/CDFs isomers are on hand in this laboratory or in any other laboratory at present. Hence, the analytical procedures described, have not been rigorously tested using all of the 136 CDDs/CDFs which comprise the tetra- thru octachlorinated dibenzo-p-dioxins and furans. However, all 22 TCDD isomers, as well as at least one of the other CDD/CDF isomers from each chlorinated class of CDDs/CDFs, are available in the Brehm Laboratory for calibration purposes. The calibration of the GC-MS-DS system also deserves special comment. As indicated above the CDDs/CDFs standards on hand were employed to obtain gas chromatographic retention time data and mass spectral data which typify a particular class of CDDs/CDFs. These data were used as the basis for establishing the GC-MS conditions appropriate for detecting and quantitating a particular class of CDDs/CDFs. As indicated above, ideally all isomers comprising a particular class of CDDs/CDFs should be available so that the retention times and mass spectral cracking patterns for each isomer could be determined. However all isomers are not available (except in certain cases such as the TCDDs) and therefore the isomers which are available of necessity are regarded as representative of the entire class. This approach may, of course, be subject to certain errors, for example, the gas chromatographic and mass spectrometric response of each isomer of a given class of CDDs/CDFs undoubtedly is slightly different and therefore one can only estimate what the retention times for each member of a particular class may be. This estimate is based in part on previous experience, and in part on other available data (for example, the relative GC retention times for other isomers in a given class). On these bases a retention time window is selected which is reasonably expected to encompass the retention times of all isomers in that class. Regarding the mass spectral behavior of isomers in a given class, it should be noted that the mass spectral ion-masses which are monitored for the quantitation of the various CDDs/CDFs all correspond to the molecular ion for that isomer (or a peak in the molecular ion isotopic cluster).

The error which may be inherent in this practice is that all isomers likely exhibit slightly different molecular ion fragmentations. However, these differences are not expected to be great (no greater than a factor of 2 difference between isomers). Finally, the actual quantitation of each CDD/CDF class is accomplished by using an internal standard technique, that is, the signal at an ion-mass typical of a particular CDD/CDF class is acquired and the peak area is obtained. The ratio of this area to the area obtained for the corresponding internal standard is calculated and the quantity of the class of CDDs/CDFs present in the sample is then calculated, taking into account the volume of extract injected, the total volume of the extract and the quantity of sample prepared for analysis. In the case of the HpCDDs, where 2 isomers are possible, the peak areas for each of these are summed during the analysis and the summed area relative to the peak area for the internal standard is obtained and the calculation of the concentration is performed as described above. In the case of the TCDFs where 38 isomers are possible, up to 38 peaks could be obtained (if it were possible to chromatographically separate all 38 isomers) and the areas of these peaks would be summed and their ratio to the internal standard would be obtained. This approach represents the current state-of-the-art of ultratrace analysis of CDDs/CDFs. No laboratory in the world possesses all of the possible CDDs/CDFs isomers and hence each laboratory can only accomplish calibrations using the standards available to that laboratory. It must be noted too, that several laboratories have unauthenticated standards or mixtures of these, (isomers which have been synthesized and identified solely on the basis of the predicted or expected products from the synthetic reaction) which are employed as calibration standards. This practice must be viewed with serious reservation until identity of the standards is confirmed either by X-ray crystallographic analyses or other interlaboratory comparative analyses.

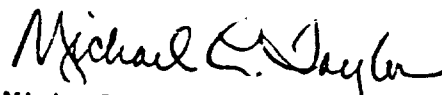
Table 3 lists the three ³⁷Cl-labelled internal standards which were employed throughout the course of these analyses. These standards, being chemically identical to the corresponding native CDDs, afford an excellent means of assessing the efficacy of the analytical methodology employed. A comparison of the quantity of each of these standards which is added to a given sample in known amount prior to processing with the quantity of this standard actually recovered is indicative of the overall reliability of the analysis. Analyses in which the recoveries of the internal standard employed were less than 50% were generally repeated (with slight modifications of methodology) until satisfactory recovery was achieved. The ³⁷Cl-labelled compounds were employed here as true internal standards, that is, the concentrations of the native compounds were determined from the ratio of the ion signal for the material to that for the added internal standard. The data listed in Table 2 are corrected for recoveries, therefore. Work is still in progress in our laboratory to characterize other organic components which may be present in these samples, as specified in the EPA work statement. These analyses should be completed and the data reported to EPA within the next two weeks.

We appreciate this opportunity to work with you and EPA. If you have questions regarding these data please don't hesitate to call us.

Sincerely,



Thomas O. Tiernan, Ph.D.
Professor of Chemistry and
Director of Brehm Laboratory



Michael L. Taylor, Ph.D.
Associate Professor of
Pharmacology/Toxicology and
Associate Director of
Brehm Laboratory

TOT/gdg

Enclosures

TABLE 1

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435
 LISTING OF SAMPLES RECEIVED FROM USEPA (CHICAGO, REGION V) 1.

EPA I.D. No.	MSU Sample No.	Description
E1205 82WT06S01	CMS-1	1 gallon of water/sediment
E1206 82WT06S03	CMS-2	3/4 gallon of water/sediment
E1208 82WT06S05	CMS-3	1 gallon of water/sediment
E1207 82WT06S07	CMS-4	3/4 gallon of water/sediment
82WT06R01	CMS-5	3/4 gallon of water/sediment

Blks

1. Samples were received on January 14, 1982. Samples were packed in styrofoam beads, and ice water was present in shipping containers. Samples CMS-2 and CMS-5 were shipped together in one container and samples CMS-1, -3 and -4 were shipped together in a second container. Caps on bottles were taped.

TABLE 2
 BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435
 CONCENTRATIONS OF TETRA- THRU OCTACHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS
 IN LEACHATE RECEIVED FROM USEPA

WSU Sample No.	CDDs/CDFs in Parts-Per-Trillion (limits of detection in parentheses)									
	TCDDs	TCDFs	PCDDs	PCDFs	HxCDDs	HxCDFs	HpCDDs	HpCDFs	OCDD	OCDF
CWS-1	0(1)	0(1)	0(2)	0(2)	4.5	6.3	86	74	323	30
CWS-2	0(1)	0(1)	0(1)	0(1)	6.3	10	181	182	675	103
CWS-3	0(1)	0(1)	0(2)	0(2)	5.8	6.3	152	112	2,693	53
CWS-4	0(1)	0(1)	0(2)	0(2)	0(3)	0(3)	0(4)	0(4)	0(6)	0(6)
CWS-5 (Field Blank)	0(1)	0(1)	0(2)	0(2)	0(3)	0(3)	0(3)	0(3)	0(6)	0(6)

*Note: See Table 1 for EPA ID match up with
 WSU sample # system C.km 3/25/82*